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The Extraction of Zirconium(IV) from Sulfuric Acid Solutions by Long-Chain Alkyl Quaternary Ammonium Compound

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Abstract

The extraction of zirconium(IV) from sulfuric acid solutions by tricaprylmethylammonium chloride (Aliquate-336, $R_3R'NCl$) in organic solvent has been investigated under different conditions. The organic phases were also examined by IR and NMR spectroscopies. As a result, it was found that Aliquat-336 extracts zirconium(IV) from sulfuric acid solutions according to the following ion-exchange reactions: $SO_4^{2-}(a) + 2R_3R'NCl(o) \rightleftharpoons (R_3R'N)_2SO_4(o) + 2Cl^-(a)$, $(R_3R'N)_2SO_4(o) + H^+(a) + HSO_4^-(a) \rightleftharpoons 2R_3R'NHSO_4(o)$, and $Zr(SO_4)_3^{2-}(a) + 2xR_3R'NHSO_4(o) + (1 - x)\ (R_3R'N)_2SO_4(o) \rightleftharpoons (R_3R'N)_2[Zr(SO_4)_3](o) + xH_2SO_4(a) + SO_4^{2-}(a)$ where $x = [R_3R'NHSO_4]/\{2[(R_3R'N)_2SO_4] + [R_3R'NHSO_4]\}$, (a) and (o) represent the aqueous and organic phases, respectively. Furthermore, the hydrolyzed species $(R_3R'N)[ZrO(OH)(SO_4)]$ is formed when zirconium is highly extracted into the organic phase.

INTRODUCTION

The separate refining of zirconium by solvent extraction has been investigated by a number of researchers (*1*). We have also studied the extraction of zirconium(IV) by organophosphorus compounds on high-molecular weight amines (*2–6*). In connection with those studies, the present paper extends the work to the extraction of zirconium(IV) from sulfuric acid solutions by a long-chain alkyl quaternary ammonium compound.

EXPERIMENTAL

Tricaprylmethylammonium chloride (General Mills, Aliquat-336, $R_3R'NCl$), used as a quaternary compound, was purified by washing several times with sodium chloride solution and *n*-hexane (*3a*). The resulting material was diluted with various organic solvents and not preequilibrated with sulfuric acid solutions. The stock solution prepared by dissolving zirconium sulfate tetrahydrate in 1.0 *M* sulfuric acid was diluted to the required concentration. Other chemicals were of analytical reagent grade.

The extraction procedures were carried out as described previously (*3a, 4, 7*). The concentrations of zirconium and sulfate were determined by titrations with EDTA using xylenol orange and Eriochrome Black T, respectively, as indicators (*8, 9*). The chloride concentration and water content of the organic phase were determined by Volhard's method and Karl Fischer titration with nitrobenzene, respectively. The acidities were determined by titration with 0.02 *M* sodium hydroxide solution using a Beckman Zeromatic pH meter, although the acidity of the organic phase was determined by adding 2 mL of the equilibrated organic phase to 25 mL of 75% ethanol.

IR spectra were determined on a Japan Spectroscopic Co. spectrometer Model IR-S, equipped with potassium chloride prisms for measurement at 4000–550 cm^{-1}, and Models IRA-1 and IR-F, the grating models for measurements at 4000–650 and 700–200 cm^{-1}, respectively, with carbon tetrachloride as reference liquid utilizing a cell with thallium halide windows and a 0.1-mm spacer. The spectra of the samples prepared by evaporation of diluent in the organic phases were also measured for a capillary film between thallium halide plates. NMR spectra were obtained as described previously (*4*).

The apparent molecular weight was determined in benzene or chloroform on a Hitachi Model 115 isothermal molecular weight apparatus.

RESULTS AND DISCUSSION

Extraction of Sulfuric Acid

In the extraction of sulfuric acid solutions at different concentrations with 0.1 *M* Aliquat-336 in benzene or chloroform at 20°C, the variation in the molar ratios of the acidity, the concentration of chloride, and water content in the organic phase to Aliquat-336 with initial aqueous sulfuric acid concentration gave the results shown in Fig. 1. Although the amount of sulfuric acid extracted by Aliquat-336 in benzene is much larger than that in chloroform, both the diluent systems exhibit that the chloride concentration in the organic phase diminishes with an increase in the initial aqueous sulfuric acid concentration, while the sulfate concentration and acidity in the organic phase increase slowly. Additionally, the acidity of the organic phase is lower than the corresponding concentration of sulfate in the organic phase at the initial aqueous $[H_2SO_4] < 0.5$ *M* for benzene and $[H_2SO_4] > 2$ *M* for chloroform,

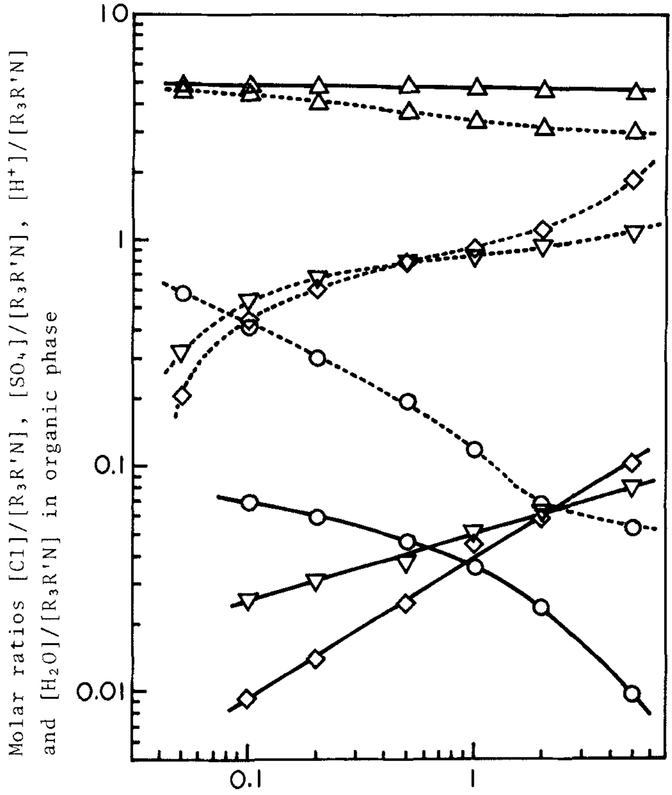

FIG. 1. Variation in the concentrations of chloride, acidity, and sulfate and water content in the organic phase with initial aqueous sulfuric acid concentration for the extraction of sulfuric acid from aqueous solutions by 0.1 *M* Aliquat-336 in chloroform or benzene. (○, ◇, ▽, and △ denote the molar ratios of $[Cl]/]R_2R'N]$, $[H^+]/[R_3R'N]$, $[SO_4]/[R_3R'N]$, and $[H_2O]/[R_3R'N]$, respectively; continuous and broken lines represent chloroform and benzene, respectively.)

but the former becomes higher than the latter above these aqueous acidities. Log-log plots of the organic sulfate concentration vs the concentration of Aliquat-336 in benzene showed slope of 0.7, 1.0, and 1.1 at the initial aqueous sulfuric acid concentration in 0.1, 1.0, and 5.0 *M*, respectively. Similar results were also obtained in the case of chloroform as diluent. This suggests that the quaternary ammonium sulfate is replaced by its bisulfate with increasing aqueous acidity. Hence it is inferred that the extraction of sulfuric acid is expressed by the equilibria (7)

$$SO_4^{2-}(a) + 2R_3R'NCl(o) \rightleftharpoons (R_3R'N)_2SO_4(o) + 2Cl^-(a) \quad (1)$$

$$(R_3R'N)_2SO_4(o) + H^+(a) + HSO_4^-(a) \rightleftharpoons 2R_3R'NHSO_4(o) \quad (2)$$

where (*a*) and (*o*) represent aqueous and organic phases, respectively. In Fig. 1, the formation of adducts such as $R_3R'NHSO_4 \cdot HSO_4$ is supported for the extraction by Aliquat-336 in benzene at higher aqueous acidities.

Further, the water content of the water-saturated quaternary compound $R_3R'NCl \cdot 5H_2O$ (*3a, 7*) diminishes with the aqueous acidity, and the compound $R_3R'NHSO_4 \cdot 3H_2O$ is formed in extraction at the initial aqueous acidity in 1 *M* Aliquat-336 in benzene. In contrast, the water content of the organic phase from the extraction by Aliquat-336 in chloroform is not reduced much because the concentration of sulfuric acid extracted by Aliquat-336 is low.

Extraction of Zirconium(IV)

Effect of Diluent. In the extraction of an aqueous solution containing zirconium sulfate (0.0035 *M*) in 0.2 *M* sulfuric acid with 0.082 *M* Aliquat-336 in various organic solvents at 20°C, the extraction efficiency of Aliquat-336 for zirconium depends on the kind of diluent: benzene (53.0) > chlorobenzene (39.2) > *o*-dichlorobenzene (27.2) > chlorobutane (21.7) ≳ 1, 2, 4-trichlorobenzene (20.8) ≳ xylene (20.4) ≳ 1, 1, 1-trichloroethane (19.9) ≳ 1, 2-dichloropropane (18.4) ≳ 1,1-dichloroethane (16.6) ≳ toluene (16.1) > 1,3-dichloroethane (14.1) ≳ carbon tetrachloride (14.0) > 1, 3-dichloropropane (10.0) > chloroform (7.02) > nitrobenzene (2.97), where the numbers in parentheses are the distribution coefficients. In a previous paper (*10*) the extraction of divalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solutions by Aliquat-336 in various organic solvents was investigated in order to obtain information on the correlation between the distribution coefficient and the physicochemical properties of the diluent. Consequently, it is found that by assuming a regular solution, the distribution coefficient and the enthalpy change associated with metal extraction are expressed in terms of the solubility parameters and the molar volumes of Aliquat-336, diluent, and the complex formed in the organic phase. However, since the diluent effect on the distribution coefficient for zirconium in the extraction of the present system differs from that of the chloride system (*3a*), there is a need to make a more detailed investigation of the diluent effect on the extraction of zirconium(IV).

Dependence on Sulfuric Acid Concentration. The extraction of aqueous solutions containing zirconium sulfate (0.0035 *M*) in sulfuric acid at various concentrations with Aliquat-336 in chloroform and benzene at 20°C gave the results shown in Fig. 1. This indicates the steep decrease of the distribution coefficients with the initial aqueous acidity, resulting either from competition between zirconium and sulfuric acid for association with the amine or from the formation of less readily extractable complexes.

This explanation is confirmed by the results in Table 1 which show data for the extraction of aqueous solutions containing zirconium sulfate (0.0035 *M*) in 0.2 *M* sulfuric acid and sodium sulfate by Aliquat-336 in chlorofom and benzene at 20°C. The results imply that when part of the sulfuric acid in the aqueous phase is replaced by sodium sulfate, the decrease in the distribution coefficient is stopped because of the reduction in sulfuric acid concentration for association with the quaternary compound.

Dependence on Concentration of Zirconium. In the extraction of aqueous solutions containing zirconium sulfate (0.0035 *M*) in 0.2 M sulfuric acid with 0.082 *M* Aliquat-336 in chloroform or 0.040 *M* Aliquat-336 in benzene at 20°C, the compositin of the organic phase as a function of initial zirconium sulfate concentration under the conditions illustrated in Table 2 approaches a limiting value of zirconium/quaternary compound/sulfate/chloride/water in the molar ratio 1:4:3:2:8 for the extraction by Aliquat-336 in chloroform, and in the molar ratio 1:1:1:0:5 for the extraction by Aliquat-336 in benzene. Accordingly, it is assumed that the stoichiometric composition of the organic phase from the extraction by Aliquat-336 in chloroform is $(R_3R'N)_4Zr(SO_4)_3 \cdot Cl_2 \cdot 8H_2O$, i.e., $(R_3R'N)_2Zr(SO_4)_3 \cdot 2R_3R'NCl \cdot 8H_2O$, because of the low extraction efficiency for zirconium. In the extraction by Aliquat-336 in benzene, however, since the extraction efficiency for zirconium is high, the hydrolyzed species (*6*) $(R_3R'N)ZrO(OH)(SO_4) \cdot 4H_2O$ is formed at higher zirconium loadings. The NMR spectral results reveal that even with the extraction by Aliquat-336 in

TABLE 1

Extraction of Zirconium(IV) from 0.2 *M* Sulfuric Acid Solutions Containing Sodium Sulfate by Aliquat-336 in Chloroform and Benzene

Diluent	[Aliquat-336] (*M*)	Distribution coefficient				
		0.2 *M*[a]	0.3 *M*	0.5 *M*	0.7 *M*	1.0 *M*
Chloroform	0.016	(0.916)	0.988	1.05	—	0.84
	0.040	(3.52)	3.59	3.66	—	2.91
	0.082	(7.58)	8.19	8.97	8.28	6.73
Benzene	0.013	(4.42)	4.01	3.61	3.59	3.14
	0.025	(10.8)	10.8	9.22	8.77	7.35
	0.062	(45.7)	39.4	32.4	30.9	26.4

[a] This indicates the initial aqueous total sulfate concentration. Parentheses denote extractions from sulfuric acid alone.

TABLE 2

Concentrations of Zirconium and Chloride and Water Content in the Organic Phase from the Extraction of Zirconium Sulfate Solutions containing 0.2 *M* Sulfuric Acid with 0.082 *M* Aliquat-336 in Chloroform or 0.040 *M* Aliquat-336 in Benzene

						Molar ratio in organic phase			
Diluent	Initial aqueous $[Zr(SO_4)_2]$ (*M*)	$[Zr]_{org}$ (*M*)	$[SO_4]_{org}$ (*M*)	$[Cl]_{org}$ (*M*)	$[H_2O]_{org}$ (*M*)	$\frac{[R_3R'N]}{[Zr]}$	$\frac{[SO_4]}{[Zr]}$	$\frac{[Cl]}{[Zr]}$	$\frac{[H_2O]}{[Zr]}$
Chloroform	0.0035	0.0028	0.0347	0.0564	0.0973	29.7	12.6	20.3	35.3
	0.0070	0.0052	0.0376	0.0533	0.108	15.9	7.33	10.3	21.0
	0.0177	0.0110	0.0459	0.0491	0.127	7.5	4.2	4.5	11.6
	0.0353	0.0168	0.0528	0.0453	0.142	4.9	3.1	2.7	8.5
	0.0882	0.0215	0.0617	0.0421	0.168	3.8	2.9	1.9	7.8
	0.177	0.0215	0.0617	0.0392	0.168	3.8	2.9	1.8	7.8
Benzene	0.0035	0.0034	0.0395	0.0063	0.130	11.8	11.6	1.9	38.1
	0.0070	0.0056	0.0422	0.0033	0.141	7.1	7.5	0.59	25.1
	0.0177	0.0136	0.0446	0.0015	0.134	2.9	3.3	0.11	9.8
	0.0353	0.0213	0.0448	0.0008	0.145	1.9	2.1	0.04	6.8
	0.0882	0.0354	0.0449	0.0005	0.166	1.1	1.3	0.01	4.7
	0.177	0.0382	0.0459	0.0003	0.182	1.0	1.2	0.008	4.8
	0.353	0.0400	0.0497	0.0001	0.193	1.0	1.2	0.002	4.8

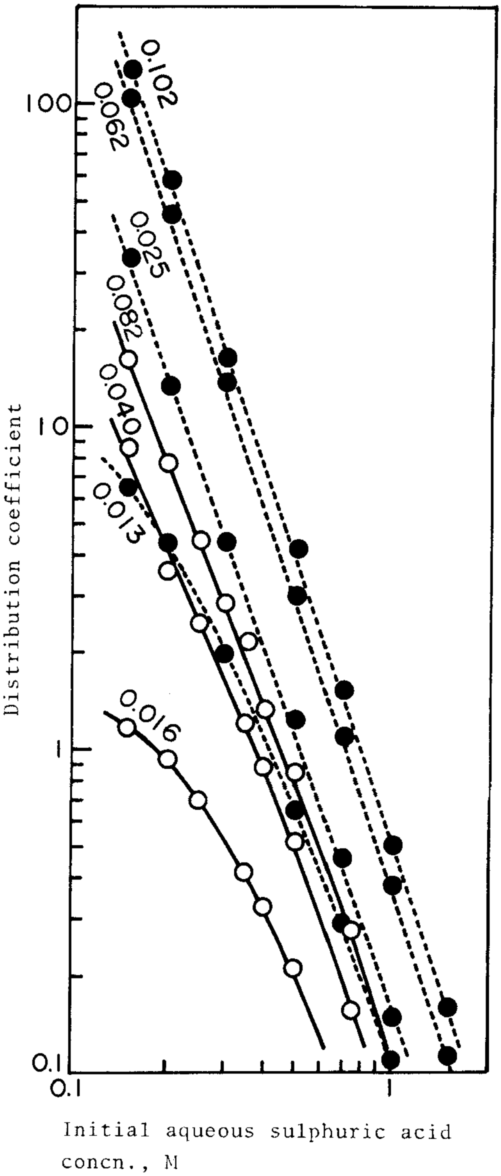

FIG. 2. Extraction of zirconium(IV) from sulfuric acid solutions by Aliquat-336 in chloroform or benzene. (Numerals on curves are Aliquat-336 concentrations, *M*; continuous and broken lines represent chloroform and benzene, respectively.)

benzene, the low zirconium loading species resembles the organic species from the extraction by Aliquat-336 in chloroform. It is therefore deduced that with increased zirconium loading, the OH-group-bearing species arises from the hydrolysis of the extracted species. Additionally, it is found that the species extracted by Aliquat-336 in carbon tetrachloride is similar to that extracted by Aliquat-336 in benzene.

Hence it is presumed that the extraction of zirconium(IV) from sulfuric acid solutions by Aliquat-336 is expressed by the following equilibrium equation (*3a, 11*):

$$\begin{aligned}&\mathrm{Zr(SO_4)_3^{2-}}(a) + 2x\mathrm{R_3R'NHSO_4}(o) + (1-x)\mathrm{(R_3R'N)_2SO_4}(o) \\ &\qquad \rightleftharpoons \mathrm{(R_3R'N)_2[Zr(SO_4)_3]}(o) + x\mathrm{H_2SO_4(a)} + \mathrm{SO_4^{2-}}(a) \qquad (3)\end{aligned}$$

where x is the equivalent fraction of bisulfate present in the uncomplexed quaternary compound, i.e., $[\mathrm{R_3R'NHSO_4}]/\{2[\mathrm{R_3R'N)_2SO_4}] + [\mathrm{R_3R'NHSO_4}]\}$. Moreover, when zirconium is highly extracted into the organic phase, the species $\mathrm{(R_3R'N)_2[Zr(SO_4)_3]}$ is hydrolyzed to form the species $\mathrm{(R_3R'N)[ZrO(OH)(SO_4)]}$.

On the other hand, the apparent weights of the compound prepared by drying zirconium-saturated organic phases from the extractions by Aliquat-336 in chloroform and benzene gave respective values of 2191 and 3560. In comparison with the theoretical values (2221 and 699, respectively), it is known that the complex from the extraction using chloroform exists in a monomer and from the extraction using benzene in a pentamer.

Dependence on Temperature. The extraction of aqueous solutions containing zirconium sulfate (0.0035 *M*) in 0.2 *M* sulfuric acid by Aliquat-336 of 0.082 *M* in chloroform and 0.025 *M* in benzene at temperatures between 10 and 50°C gave the results shown in Table 3. The increase in distribution coefficient with rising temperature is analogous to that for zirconium from hydrochloric acid solutions (*3a*). The heats of reaction (change in enthalpy, $-\Delta H$) were estimated to be -17.4 and -3.9 kJ/mol in chloroform and benzene, respectively.

IR Spectra. The organic phases from the extraction of aqueous solutions containing zirconium sulfate (0.0035, 0.0070, 0.0353, 0.0882, and 0.177 *M*) in 0.2 *M* sulfuric acid with 0.082 *M* Aliquat-336 in carbon tetrachloride at 20°C were examined by IR spectrophotometry. The spectra of the compounds freed from organic solvent by evaporation resemble those in the organic solvent with minor differences in the peak frequencies and intensities.

TABLE 3

Extraction of Zirconium(IV) from 0.2 *M* Sulfuric Acid Solution by Aliquat-336 in Benzene or Chloroform

	Distribution coefficient	
Temperature (°C)	0.025 *M*[a]	0.082 *M*[b]
10	12.8	6.11
20	13.2	7.58
30	13.9	8.80
40	14.6	13.0
50	16.0	15.3

[a] The concentration of Aliquat-336 in benzene.

[b] The concentration of Aliquat-336 in chloroform.

For the extraction of 0.2 *M* sulfuric acid, the bands assinged to the vibrations of the bisulfate ion (*12, 13*) appear at 1215, 1180, 1045, and 860 cm^{-1} in addition to the adsorptions due to Aliquat-336 (*7*). In contrast, the organic phases from the extraction of zirconium sulfate solutions exhibit absorptions attributable to the quaternary ammonium compound—zirconium sulfate complex. With increasing aqueous sulfate, the bands at 1210, 1140–1110, 985, 955 cm^{-1}, assigned to a sulfato group (*12, 14*) coordinated with the zirconium as a bidentate ligand (point group C_{2v} symmetry), show a progressive increase in intensity, whereas the absorptions of the bisulfate ion resulting from the extraction of sulfuric acid become weaker. Furthermore, the organic extracts from aqueous solutions at higher zirconium sulfate concentrations reveal the Zr-O Stretching band (*6*) at 450 cm^{-1}, ascribed to the formation of the hydrolyzed species $(R_3R'N)[ZrO(OH)(SO_4)(H_2O)_4]$.

NMR Spectra. The organic phases from the extraction of zirconium sulfate solutions (0.007, 0.0177, 0.0353, and 0.177 *M*) in 0.2 *M* sulfuric acid with 0.082 *M* Aliquat-336 in carbon tetrachloride at 20°C were examined by NMR spectroscopy. Similar experiments were carried out for the extraction of a 0.2 *M* sulfuric acid solution alone.

The NMR spectrum for Aliquat-336 shows a peak at 9.12 (τ value) in a triplet from the methyl protons, a strong peak at 8.69 assigned to methylenic protons, and a peak at 6.56 due to the methylenic and methyl protons attached to the nitrogen atom (*15*). For a water-saturated quarternary compound, the water proton resonance appears at 6.01 as a sharp peak, and the signal from the methylenic and methyl protons attached to the nitrogen atom is shifted to a higher field at 6.77. In the extraction of 0.2 *M* sulfuric acid alone, the water proton signal at 6.01 is shifted to a lower field at 5.50, ascribed to the formation of a stronger hydrogen bond in replacing part of the compound $R_3R'NCl \cdot 5H_2O$ by the compound $R_3R'NHSO_4 \cdot 3H_2O$.

The spectra of the organic solutions from the extraction of zirconium sulfate solutions show that the water proton signal at 5.50 shifts to higher fields at 5.64 and 5.74 for the initial aqueous zirconium concentrations at 0.0070 and 0.0177 *M*, respectively, and simultaneously the intensity in both peaks decreases, suggesting the lowering of a hydrogen bond in the organic phase by the formation of the extracted species $(R_3R'N)_2[Zr(SO_4)_3(H_2O)_2]$. In the extractions of zirconium sulfate solutions at higher initial aqueous zirconium concentrations at 0.0353 and 0.177 *M*, the water proton signal shifts to lower fields at 5.63 and 5.20, respectively, and at the same time their signals become broad. This phenomenon is attributed to the formation of the hydrolyzed species $(R_3R'N)[ZrO(OH)(SO_4)(H_2O)_4]$ in the polymer.

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REFERENCES

1. E.g., M. Zdeneki, D. Schrotterva, U. Jedinakova, M. Munka, and J. Celeda, *Proc. Int. Solvent Extraction Conf., Lyon, 1974*, Vol. 1, Soc. Chem. Ind., London, 1974 p. 447; R. Shabana and F. Hafeg, *J. Radioanal. Chem., 29*, 99 (1976); S. Tribalat and L. Schriver, *J. Inorg. Nucl. Chem., 38*, 145 (1976).
2. T. Sato, *Z. Anorg. Allgem. Chem.*, 367, 303 (1969); T. Sato, *Anal. Chim. Acta, 52*, 183 (1970); T. Sato and T. Nakamura, *J. Inorg. Nucl.* Chem., *33*, 1081 (1971).
3. (*a*) T. Sato and H. Watanabe, *Anal. Chim. Acta, 49*, 463 (1970); (*b*) *54*, 439 (1971).
4. T. Sato and H. Watanabe, *J. Inorg. Nucl. Chem., 36*, 2585 (1974).
5. T. Sato and H. Watanabe, *Thermochim. Acta, 31*, 159 (1979).
6. T. Sato, H. Watanabe, S. Kotani, M. Yamamoto, and M. L. Good, *Anal. Chim. Acta, 84*, 397 (1976).
7. T. Sato, H. Watanabe, and S. Kikuchi, *J. Appl. Chem. Biotechnol., 25*, 633 (1975).
8. J. Kinnunen and B. Wennerstrand, *Chemist-Analyst, 46*, 92 (1957).
9. K. F. Sporek, *Anal. Chem., 30*, 1032 (1958).
10. T. Sato, T. Shimomura, T. Nakamura, and T. Fujimatsu, *Proc. Int. Solvent Extraction Conf., Liège, 1980*, Vol. 3, 1980, pp. 80–183.
11. T. Sato, *J. Appl. Chem., 12*, 130 (1962); *13*, 254 (1963).
12. T. Sato, *J. Inorg. Nucl. Chem., 24*, 1267 (1962); *25* 441 (1963).
13. G. E. Walrafen and D. M. Dodd, *Trans. Faraday Soc., 57*, 1286 (1961).
14. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compound*, 3rd ed., Wiley-Interscience, New York, 1977, p. 239.
15. T. Sato, *J. Inorg. Nucl. Chem., 34*, 3835 (1972).

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